

Acid Catalyzed Competitive Esterification and Ketalization of Levulinic Acid with 1,2 and 1,3-Diols: The Effect of Heterogeneous and Homogeneous Catalysts

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Abstract Condensation reactions of levulinic acid (LA) with 1,2-ethanediol (1,2-ED), 1,2-propanediol (1,2-PD), and 1,3-propanediol (1,3-PD) were studied using Amberlyst-15 as well as *p*-toluenesulfonic acid catalysts in benzene under Dean-Stark conditions. In Amberlyst-15 catalyzed reactions the products are ketals and ketal-esters, whereas *p*-toluenesulfonic acid catalyzed reactions produce esters and ketal-esters as products. In *p*-toluenesulfonic acid catalyzed reactions with 1,2-ED and 1,3-PD, LA monoester product is formed as the major product after 180 min in 75 and 97 % yields respectively. Unlike the previously reported acid catalyzed ketalization of ethyl levulinate with diols, combined ketalization–esterification of LA with diols is a complex process.

Graphical Abstract

1 Introduction

Levulinic acid (LA) or 4-oxopentanoic acid is a key renewable chemical since this C-5 feedstock can be produced from the most abundant biopolymer cellulose via a series of acid catalyzed reactions [1]. This keto-acid was listed as one of the top 12 most promising value added chemicals from biomass by the Biomass Program of the US Department of Energy in 2004 [2] and continues to rank highly in more recent reviews of major biorefinery target products [3]. Even though the current global LA consumption is around 2600 tons/year, it is expected to increase steadily in the coming years, especially due to the introduction of the Biofine process, which has been pro-



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jected to lower LA costs to as low as 0.09–0.22 \$/kg [4]. This versatile building block can be used in the synthesis of various organic chemicals such as levulinate esters, 2-methyl THF, γ -valerolactone, acrylic acid, 1,4-pentanediol, β -acetylacrylic acid, α -angelica lactone, δ -amino levulinic acid, etc. [4, 5]. LA and its derivatives have been used as building blocks for the preparation of polymers

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[6–8]. For example, 5-hydroxylevulinic acid derived from LA has been used as the monomer for the preparation of poly(5-hydroxylevulinic acid) and biodegradable poly(5-hydroxylevulinic acid-*co*-L-lactic acid) [7, 8].

Bifunctional LA can undergo ketalization as well as esterification with polyhydric alcohols like 1,2 and 1,3diols. We have recently explored this behavior in the synthesis of a polymeric product by the condensation of LA with another renewable resources based material glycerol to give an oligomer of DP ~ 10 [6]. The ketalization of levulinate esters is also a current topic as trans-esterification was not observed in the ketalization of ethyl levulinate with polyols 1,2-ethanediol, trimethylol propane and glycerol under low acid concentration conditions [9]. In a similar study, Freitas et al. recently reported the acid-catalyzed ketalization of ethyl levulinate with 1,2-dodecanediol using different acid catalysts such as; p-toluenesulfonic acid, Amberlyst-70, zeolite H-ZSM-5, and niobium phosphate. Good activity and recyclability of the heterogeneous catalysts were ascertained in the reaction with longer-chain 1,2-dodecanediol [10]. In addition, levulinate ketal-esters can be prepared directly by acid catalyzed degradation of glucose or cellulose in a aqueous diol medium as well [11-13]. For example, we have recently shown that a mixture of 2-hydroxyethyl levulinate, 2-hydroxyethyl levulinate ethylene ketal, and 2,3,6,7-tetrahydro-cyclopenta[1,4]dioxin-5-one are formed during the liquefaction of cellulose in ethylene glycol at 180 °C, using 1-(1-alkylsulfonic)-3-methylimidazolium chloride ionic liquids as catalysts.

In recent years, LA ketals and esters have attracted attention as biodegradable surfactants [10] as well as polymer additives [9]. However, the direct condensation of LA with polyols and the effect of type of acid catalyst on the competing ketalization and esterification processes are not reported in the literature. In continuing our efforts in developing catalytic methods for the production of LA derived new feedstock materials, we have studied the solid acid Amberlyst-15 as well as *p*-toluenesulfonic acid catalyzed condensations of LA with 1,2-ethanediol (1,2-ED), 1,2-propanediol (1,2-PD), and 1,3-propanediol (1,3-PD), as shown in Fig. 1 [14–18].

2 Experimental

2.1 Materials and Instrumentation

LA, 1,2-ED (99 %), 1,2-PD (>99 %), 1,3-PD (>99 %), Amberlyst-15 hydrogen form (4.7 meq/g by dry weight), *p*toluenesulfonic acid monohydrate (99 %) and anhydrous benzene were purchased from Aldrich Chemical Co. ¹H NMR Spectra were recorded in CDCl₃ on a Varian Mercury plus spectrometer operating at 400 MHz and chemical shifts are given in ppm downfield from TMS ($\delta = 0.00$). ¹³C NMR were recorded in the same spectrometer at 100 MHz, and chemical shifts were measured relative to CDCl₃ and converted to δ (TMS) using δ (CDCl₃) = 77.00.

2.2 General Procedure for Acid Catalyzed Esterification and Ketalization of LA with 1,2 and 1,3-diols

LA (116 mg, 1.00 mmol), diol (10 mmol), Amberlyst-15 hydrogen form or *p*-toluenesulfonic acid (0.047 mmol H^+) were added to 20.0 mL of benzene in a Dean–Stark apparatus and heated under reflux. Then 1.00 mL samples



Fig. 1 Acid catalyzed condensation of levulinic acid (LA, 1) with diols (2a-c) to give ketal (K, 3a-c), ester (E, 4a-c), and ketal-ester (KE, 5a-c) products

were withdrawn at t = 10, 20, 40, 80, 180 and 360 min into vials and solvent was evaporated under reduced pressure. The residue was analyzed by recording NMR spectra in CDCl₃. The percent compositions of the samples withdrawn were calculated by manual integration of methyl and methylene ¹H NMR peaks of unreacted LA, ketal (K), ester (E), and ketal-ester (KE). A representative ¹H NMR spectrum of the sample withdrawn after 20 min from the Amberlyst-15 catalyzed reaction of LA, with 1,2-ED is shown in Fig. 2. This spectrum shows unreacted LA as well as the formation of K and KE products.

The mol% of unreacted LA in the sample was calculated using peak areas corresponding to 2H's and the formula:

mol% levulinic acid (LA)

$$=\frac{\text{peak area at } 2.76 \text{ ppm}}{\text{peak area at } 2.76 \text{ ppm} + \text{peak area at } 2.43 \text{ ppm}} \times 100\%$$

The mol% of KE in the sample was calculated using the formula:

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mol% ketal-ester (KE)
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min

$$=\frac{\text{peak area at 4.24 ppm}}{\text{peak area at 2.76 ppm} + \text{peak area at 2.43 ppm}} \times 100\%$$

The mol% of K in the sample was calculated using the formula:

mol% ketal (K) =
$$100 - [\%$$
 levulinic acid (LA)
+ % ketal-ester (KE)]

Similar equations were used in the calculation of product mol% compositions and unreacted mol% of LA in the reactions carried out with 1,2-ED, 1,2-PD and 1,3-PD using two acid catalysts. The results showing the changes in product mol% composition and unreacted mol% LA in six experiments are shown in Fig. 3, plots a-f.

3 Results and Discussion

The acid catalyzed condensation reaction of LA, with three diols: 1,2-ED, 1,2-PD and 1,3-PD were studied as shown in Fig. 1. Two sets of reactions were carried out using Amberlyst-15 and *p*-toluenesulfonic acid as catalysts with the same H⁺ loading under identical conditions, in order to compare the effect of heterogeneous and homogeneous catalysts on the condensation reactions. An excess of diol (LA: diol 1:10 mol ratio) was used in all experiments to minimize the formation of di-ester type products. The changes in mol% composition with time was analyzed by withdrawing small samples from the reaction mixture at t = 10, 20, 40, 80, 180 and 360 min and recording NMR spectra in CDCl₃ after removal of benzene. The products formed in the reactions and unreacted levulinic acid in analyzed samples were identified by comparison of ¹H and ¹³C NMR data with published data of these compounds [19, 20]. A representative ¹H NMR spectrum of a sample withdrawn after 20 min from Amberlyst-15 catalyzed condensation of levulinic acid (LA, 1) with 1,2-ethanediol



a LA + 1,2-ED (Amberlyst-15)

















d LA + 1,2-ED (*p*-TsOH)







◄ Fig. 3 The changes in mol% composition with time in Amberlyst-15 and *p*-toluenesulfonic acid catalyzed condensation reactions of levulinic acid (LA) with 1,2-ethanediol (1,2-ED) 1,2-propanediol (1,2-PD) and 1,3-propanediol (1,3-PD). Solvent: Benzene, reflux in Dean–Stark water separator

(1,2-ED, 2a) to give ketal (K, 3a), and ketal-ester (KE, 5a) products is shown in Fig. 2. In the proton NMR spectrum the CH₃ group of unreacted LA can be observed as a singlet at 2.20 ppm, whereas two small triplets at 2.62 and 2.76 ppm corresponds to the methylene protons of LA. The ketal (K, 3a) and ketal-ester (KE, 5a) are the only products formed in this reaction and the strong absorption from two overlapped triplets at 2.43 ppm can be assigned to a set of $-CH_2$ - groups from ketal (K, 3a), and ketal-ester (KE, 5a). The other $-CH_2$ - signals from these two products are observed as a pair of close triplets at 2.09 and 2.04 ppm. The two triplets at 3.80 and 4.23 ppm can be assigned to $-CH_2$ -OH and $-CH_2$ -OCO methylene groups of the ketal-ester.

The mol% of unreacted LA, as well as KE and K in the sample were calculated using ¹H NMR peak areas and formulas as shown in section "General procedure for acid catalyzed esterification and ketalization of levulinic acid with 1,2 and 1,3-diols". Similar equations were used in calculation of product mol% compositions and unreacted mol% of LA in the reactions carried out with 1,2- 1,2-ED, 1,2-PD and 1,3-PD using two acid catalysts. The results showing the changes in product mol% compositions and unreacted mol% LA in six experiments are shown in Fig. 3, plots a–f.

In Amberlyst-15 catalyzed reactions the products are K and KE, whereas the *p*-toluenesulfonic acid catalyzed reactions produced esters and KE as products. In all Amberlyst-15 catalyzed reactions KE is the major product after ~ 180 min. In Amberlyst-15 catalyzed set, the reaction of 1,2-ED with LA showed the most rapid decrease in LA concentration. In this reaction, the mol% of K increased rapidly in the first 20 min. Therefore 88 % yield of K product can be obtained in the 1,2-ED reaction after 20 min of reaction using Amberlyst-15 catalyst. However, as the reaction progresses, the K reacts with excess 1,2-ED producing KE as the major product, and comes to an equilibrium between KE and K after about 180 min. In comparison of the heterogeneous Amberlyst-15 and homogeneous p-toluenesulfonic acid, heterogeneous catalyst promotes more K formation whereas the homogeneous catalyst promotes the E formation. In the *p*-toluenesulfonic acid catalyzed reactions with linear alcohols 1,2-ED and 1,3-PD the esters are formed as major products after 180 min in 75 and 97 % yields respectively; however with the branched diol 1,2-PD ester yield is only 7 % after 180 min. This may be due to a slowdown in the esterification due to steric hindrance in branched diol 1,2-PD and at the same time competitive ketalization promotes the formation of KE as the major product in 88 % yield after 180 min.

4 Conclusion

Ketalization and esterification are competing processes in acid catalyzed condensation of LA with 1,2 and 1,3-diols. In Amberlyst-15 catalyzed reactions the products are K and KE, whereas *p*-toluenesulfonic acid catalyzed reactions produced E and KE. Unlike the previously reported acid catalyzed ketalization of ethyl levulinate with diols, one-pot combined ketalization–esterification of LA with diols is a complex process. The highest K yield of 88 % was obtained in a experiment with 1,2-ED using Amberlyst-15 catalyst. The highest KE (88 %) and E (97 %) yields were obtained in experiments with 1,2-PD and 1,3-PD respectively, using *p*-toluenesulfonic acid catalyst.

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